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Dedicated to V.F. Mironov on His 60th Anniversary

Synthesis of New *p-tert*-Butylcalix[4]arene Derivatives Containing Photopolymerizable 1,3-Butadiyne Fragments

V. A. Burilov[a]*, A. M. Valiyakhmetova[a], R. I. Aukhadieva[a], S. E. Solovieva[a, b], and I. S. Antipin[a,b]

[a] *Kazan (Volga region) Federal University, ul. Kremlevskaya 18, Kazan, Tatarstan, 420008 Russia*
**e-mail: ultrav@bk.ru*

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, Tatarstan, 420008 Russia*

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Abstract—Successive functionalization of *p-tert*-butylcalix[4]arene afforded a bifunctional derivative containing photopolymerizable pentacosa-10,12-diynoic acid fragments on the upper rim and propargyl groups on the lower rim of the macrocycle having a cone structure. The functionalization can be readily accomplished via copper-catalyzed azide–alkyne cycloaddition under mild conditions.

Keywords: *p-tert*-butylcalix[4]arene, polydiacetylenes, copper-catalyzed azide–alkyne cycloaddition (CuAAC)

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Polymeric materials capable of changing their spectral characteristics under external mechanical action attract increasing attention of researchers [1, 2]. Among such polymers, a particular place is occupied by polydiacetylenes. Polydiacetylenes can be obtained from various self-organizing buta-1,3-diyne monomers by simple photopolymerization [3]. Functional materials based on polydiacetylenes are widely used in colorimetric determination of metal ions [4], organic molecules [5], biomolecules [6], and bacteria [7]. They are sensitive to variation of pH [8] and temperature [9]. The key mechanism of colorimetric response involves change of the geometry of polymer chain which leads to distortion of the polymer π-conjugation system and hence changes the color (as a rule, from blue to red) and fluorescence properties [10]. The nature of functional groups on the polymer surface is crucial for the design of colorimetric sensors for various analytes.

Sensor devices based on polydiacetylenes are created according to two main approaches. The first approach involves covalent conjugation of a receptor block with commercially available pentacosa-10,12-diynoic acid through an amide bond with subsequent synthesis of conjugates and their photopolymerization [11]. The second approach implies non-covalent functionalization of pentacosa-10,12-diynoic acid with amphiphiles which are added before polymerization of conjugates [12]. The second approach is the simplest one, and covalent conjugation of a receptor block with diacetylene matrix could enhance the sensitivity of conjugates.

It seemed promising to fix functional derivatives of calix[4]arene on the surface of polydiacetylene matrix, taking into account that the ability of calixarenes to bind various molecules is successfully utilized in the design of various extractants, highly efficient receptors, and molecular devices [13, 14]. However, covalent conjugates of *p-tert*-butylcalix[4]arene and its derivatives with a polydiacetylene matrix have been reported in a single publication [15], and the conjugation was achieved through an ester bond which is hydrolytically unstable in acidic and alkaline media. We previously synthesized bifunctional 1,3-*alternate* *p-tert*-butylthiacalix[4]arene derivatives possessing polymerizable buta-1,3-diyne fragments at one side of the macrocycle cavity and azide groups [introduced for subsequent functionalization via copper-catalyzed azide–alkyne cycloaddition (CuAAC)], at the other side [16]. On the basis of tetracarboxytriazolyl *p-tert*-butylthiacalix[4]-arene derivatives we obtained polydiacetylene con-